

PATENT SPECIFICATION

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(54) HAIR SHAMPOO

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E/C 4, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a hair shampoo having improved sebo-static or sebo-repressing activity.

It is generally known that seborrhoea of the human scalp is a serious problem. Seborrhoea of the scalp is caused by excessive secretion of the sebaceous glands, the result of which is that the hair, after being washed, becomes rapidly greasy again and consequently wispy and untidy in appearance.

The object of the invention therefore is to provide a hair shampoo by which a significant decrease of subsequent or recurrent greasing is obtained.

This object is achieved in that it was found that hair shampoos with a pH within a specific range, which contain glycyrrhizin or salts thereof, cause a substantial decrease of recurrent greasing of the hair treated with them. Whereas on applying conventional hair shampoos renewed grease formation will often set in even after two days, the result of hair washing with the shampoos according to the invention — depending on which type of glycyrrhizin is used — is that grease formation may only recur after five days.

Accordingly the present invention relates to hair shampoo having sebo-static or sebo-repressing action, containing from 0.1—10% by weight of glycyrrhizin or a potassium, ammonium or calcium salt thereof, and from 5—90% by weight of a detergent-active material, the shampoo having a pH within the range of 5.0—9.0.

Glycyrrhizin is a compound, known per se, and is the glycoside of 1 mole glycyrrhetic acid and 2 moles glucuronic acid. According to the invention

glycyrrhizin can be used either as such or in the form of its potassium, ammonium or calcium salts. For the purpose of the invention the ammonium salt is preferred.

The proportion of glycyrrhizin or salts thereof to be used is of course dependent on the purity of the product; in general, however, the proportion thereof is in the range of 0.1—10, preferably between 0.25—5, in particular between 0.5—1.5% by weight, calculated on the hair shampoo.

The pH required for the hair shampoo according to the invention is between 5.0 and 9.0, preferably between 6.0 and 8.0.

The shampoo according to the invention may be formulated into an aqueous or aqueous/alcoholic solution; it may also be applied in the form of a gel by means of suitable thickening agents or it may be administered in the form of a spray. It is preferred that the shampoos of the invention do not contain reducing agents of the type used in cold permanent wave compositions, such as thioglycolates or cysteine hydrochloride, as these may interfere with the sebo-static or sebo-suppressing action of the glycyrrhizin or the salts thereof. The shampoo of the invention comprises in addition to glycyrrhizin or salts thereof a detergent-active material. Examples of such detergent-active materials are anionic surfactants such as alkylaryl sulphonates, alkyl- and alkylarylether sulphonates, alkyl sulphates, sarcosides, fatty acid alkylolamide sulphates, sulphuric acid esters of monoglycerides, peptide fatty acid condensates, alkylpolyglycolether carboxylic acids, alkyl- and alkylether phosphates, and alpha olefin sulphonates. Also cationic surfactants may be used, such as quaternary ammonium compounds, as well as ampholytic surfactants such as betaines and sulpho-betaines, alkylamino carboxylic acids and imidazoline derivatives. Further, nonionic surfactants may be used, such as for instance fatty alcohol polyglycolethers, fatty acid polyglycol esters, alkylphenol-polyglycols, ethoxylated amides and amines. Furthermore also tertiary amine-

oxides may be used. The proportion of detergent-active material amounts in general to 5 to 90% by weight, preferably 10—80% by weight.

- 5 The shampoos according to the invention may further contain the usual additives as e.g. thickening agents, foam improvers, foam stabilizers, conditioning agents, anti-static agents, pH controllers, opacifiers and
10 gloss improving agents, solubilizers,

perfumes, preservatives and colourants. The preferred shampoos are liquid aqueous compositions according to the invention.

The present invention is further illustrated by the following examples.

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Example I.

The following liquid shampoos were prepared:

	wt. %	
	A	B
Sodium lauryl ethersulphate	70.0	70.0
Coconut fatty acid diethanolamide	2.0	2.0
Formalin	0.1	0.1
Perfume	0.5	0.5
NaCl	3.0	4.0
Distilled water	24.38	22.4
Citric acid	0.02	—
Ammonium glycyrrhizinate (100% active ingredient)	—	1.0
pH-value	6.9	6.7

- 20 Each shampoo was used one time by a test panel of 40 members, who had very greasy hair; subsequently the results on the hair were observed over a 12 days' period, without the hair being washed again during
25 this period. With product A recurrent grease formation could be observed even

after one day, whereas with product B recurrent greasing could be observed only after six days.

Example II.

The shampoos in Table I were prepared:

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TABLE I

	A	B	C	D	E	F	G	H
	wt. %							
Sodium lauryl ethersulphate		70.0						
Coconut fatty acid diethanolamide		2.0						
Formalin		0.1						
Perfume		0.3						
NaCl	0.5	0.3	1.5	1.3	4.0	3.0	4.5	4.5
Colourants	0.35	0.35	-	-	0.35	0.35	0.35	0.35
Distilled water	24.45	24.35	13.75	12.6	21.04	22.0	19.5	18.65
K/Ca-glycyrrhizinate (5%) (unpurified)	-	-	11.0	-	-	-	-	-
Ammonium glycyrrhizinate (5%)	-	-	-	11.0	-	-	-	-
Ammonium glycyrrhizinate (100%)	-	-	-	-	1.0	1.0	1.0	1.0
Disodium monohydrogen phosphate 2.H ₂ O	-	-	1.2	-	1.0	0.3	1.5	1.8
Potassium dihydrogen phosphate	2.0	-	0.05	-	0.06	0.7	-	-
Diammonium monohydrogen phosphate	-	0.3	-	0.2	-	-	-	-
Triammonium phosphate	-	1.6	-	1.8	-	-	-	-
Sodium hydroxide (10%)	0.3	-	0.1	-	0.15	0.25	0.75	1.3
Hydrogen chloride	-	0.7	-	0.7	-	-	-	-
pH-value	6	8	8	8	7	6	8	9

The above shampoos were each tested by a panel of 25 members, who showed fairly severe scalp and hair greasing (age of test members in each group were 24—45 years; men: women about 50:50). The washing tests were so arranged that as many shampoos as possible were tested under analogous conditions so as to exclude climatic influence as much as possible. The treatment was effected in such a way that during six weeks one hair washing was performed once a week. The initial assess-

ment, which preceded the issue of shampoo, was made by personnel who were experts in the assessment of human scalp and hair. At the end of the six weeks' treatment the extent of recurrent grease formation of scalp and hair was subjected for 10 days to a visual and manual assessment. The following results were obtained:

Recurrent grease formation of scalp and hair of the head after one weekly hair washing performance over a period of six weeks.

Shampoo	Numbers of testers	Number of testers with grease formation back at starting value										days after last treatment
		1	2	3	4	5	6	7	8	9	10	
A	25	9	12	3	1	—	—	—	—	—	—	
B	25	4	12	8	1	—	—	—	—	—	—	
C	25	—	—	5	2	10	8	—	—	—	—	
D	25	—	1	3	3	8	8	1	1	—	—	
E	25	—	—	—	1	1	8	12	3	—	—	
F	25	—	—	—	2	3	6	8	4	2	—	
G	25	—	—	—	2	2	4	15	2	—	—	
H	25	—	—	—	2	12	8	3	—	—	—	

These results show that on using shampoos A and B, which contained no glycyrrhizinate, grease formation had returned to the initial value even after 1—2 days. With shampoos C—H grease formation was back at starting value only after 5—7 days. Recurrent grease formation was therefore substantially reduced by the use of the shampoos of the invention, as compared with placebos A and B.

On comparing shampoos F, E, G and H (pH values 6, 7, 8 and 9) it was found that shampoos F, E and G showed a comparable effect and that shampoo H was relatively less effective. Moreover, on using shampoo F it was found that the hair could be very easily dressed.

Example III:

In the manner as described in Example II, shampoos F, E, G (pH values 6, 7 and 8) were compared with shampoo I. I was identical to the other shampoos, except that it did not contain $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ nor NaOH , and that its pH was adjusted with HCl to 4.

The test-period was 14 days, and the hair-washing took place twice a week. The results showed that with shampoo I grease formation returned to the initial value after two days with 5% of the testers, after three days with another 5% of the testers, and after four days with another 10% of the

testers. With the shampoos F, E and G no grease formation occurred at all until after four days, when 8, 4 and 8% of the testers showed grease formation.

Example IV.

A test as described in Example III with three identical shampoos as composition G, having a pH of 8, but with 0.3, 0.5 and 1.0% ammonium glycyrrhizinate showed a relative increase in effectiveness of the same order.

Example V.

Using higher amounts of ammonium glycyrrhizinate in Example I B, e.g. 1.5, 2 and 5%, produced similar results, but at the higher concentrations the appearance of the hair becomes cosmetically less attractive.

WHAT WE CLAIM IS:—

1. A hair shampoo having sebostatic and sebo-repressing activity, containing from 0.1—10% by weight of glycyrrhizin or a potassium, ammonium or calcium salt thereof, and from 5—90% by weight of a detergent-active material, the preparation having a pH within the range 5.0—9.0.

2. A shampoo according to claim 1, containing from 0.5—1.5% by weight of ammonium glycyrrhizinate.

3. A shampoo according to claim 1 or 2, substantially as described in the Examples. 5
having a pH value within the range 6.0—8.0.
4. A hair shampoo, comprising a
glycyrrhizinate and having a pH of 5—9,

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